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OXIDATION OF ORGANIC COMPOUNDS

FIELD OF THE INVENTION

The present invention relates to the in situ and ex situ oxidation of organic compounds in soils, groundwater, process water and wastewater and especially relates to the in situ oxidation of volatile and semi-volatile organic compounds, pesticides and herbicides, and other recalcitrant organic compounds in soil and groundwater.

BACKGROUND OF THE INVENTION

The presence of volatile organic compounds (VOCs), semi volatile organic compounds (SVOCs) or pesticides in subsurface soils and groundwater is a well-documented and extensive problem in industrialized and industrializing countries. Many VOC's and SVOC's are compounds which are toxic or carcinogenic, are often capable of moving through the soil under the influence of gravity and serving as a source of water contamination by dissolution into water passing through the contaminated soil. These include, but are not limited to, chlorinated solvents such as trichloroethylene (TCE), vinyl chloride, tetrachloroethylene (PCE), methylene chloride, 1,2-dichloroethane, 1,1,1-trichloroethane (TCA), carbon tetrachloride, chloroform, chlorobenzenes, benzene, toluene, xylene, ethyl benzene, ethylene dibromide, methyl tertiary butyl ether, polyaromatic hydrocarbons, polychlorobiphenyls, phthalates, 1,4-dioxane, nitrosodimethyl amine, and methyl tertbutyl ether.

In many cases discharge of these compounds into the soil leads to contamination of aquifers resulting in potential public health impacts and degradation of groundwater resources for future use. Treatment and remediation of soils contaminated with VOC or SVOC compounds have been expensive, require considerable time, and in many cases incomplete or unsuccessful. Treatment and

remediation of volatile organic compounds that are either partially or completely immiscible with water (i.e., Non Aqueous Phase Liquids or NAPLs) have been particularly difficult. Also treatment of highly soluble but biologically stable organic contaminants such as MTBE and 1,4-dioxane are also quite difficult with conventional remediation technologies. This is particularly true if these compounds are not significantly naturally degraded, either chemically or biologically, in soil environments. NAPLs present in the subsurface can be toxic to humans and other organisms and can slowly release dissolved aqueous or gas phase volatile organic compounds to the groundwater resulting in long-term (i.e., decades or longer) sources of chemical contamination of the subsurface. In many cases subsurface groundwater contaminant plumes may extend hundreds to thousands of feet from the source of the chemicals resulting in extensive contamination of the subsurface. These chemicals may then be transported into drinking water sources, lakes, rivers, and even basements of homes through volatilization from groundwater.

The U.S. Environmental Protection Agency (USEPA) has established maximum concentration limits for various hazardous compounds. Very low and stringent drinking water limits have been placed on many halogenated organic compounds. For example, the maximum concentration limits for solvents such as trichloroethylene, tetrachloroethylene, and carbon tetrachloride have been established at 5 .mu.g/L, while the maximum concentration limits for chlorobenzenes, polychlorinated biphenyls (PCBs), and ethylene dibromide have been established by the USEPA at 100 .mu.g/L, 0.5 .mu./L, and 0.05 .mu.g/L, respectively. Meeting these cleanup criteria is difficult, time consuming, costly, and often virtually impossible using existing technologies.

The literature teaches the use of strong oxidizing agents to treat contaminated soil by chemically degrading recalcitrant and hazardous chemicals, either *in situ* or *ex situ*. Such oxidizers include Fenton's reagent, ozone, potassium permanganate and

persulfates. One key aspect to the ability of an oxidizer to function is its ability to permeate through the subsurface, interacting with target compounds throughout the entire zone of contamination. Oxidizing species, such as peroxide,ozone and hydroxyl radicals have relatively short lifetimes within the subsurface. Persulfate radicals survive for greater periods. However there is a desire to have even longer lived active species available for organic species decomposition in order to increase the zone or reaction, without resorting to multiple injection points throughout the contamination area.

It is commonly known that the reactivity of hydrogen peroxide, through the production of hydroxyl radicals, requires acid conditions. Typically acid is added with the hydrogen peroxide to increase the rate of reaction. Also, in many of its idustrial uses, persulfate solutions are also kept under acidic conditions to increase their reactivity.

Persulfates have been shown to oxidize a wide range of recalcitrant chemicals, and in combination with either heat or catalyst, are highly effective. However, it is known that during the course of oxidation by persulfate, the persulfate decomposition and reaction pathways generate sulfuric acid. One part of persulfate produces one part of sulfuric acid. If the buffering capacity of the nascent soil is not high enough, this acid production may yield a lowering of the ambient pH. While the acidic pH aids in the reactivity of the persulfate, low soil or ambient pH in the groundwater can be an issue, particularly resulting in the mobilization of toxic metals in the subsurface, causing an increase in oxidant decomposition rates, or requiring further remediation to meet regulated pH guidelines.

SUMMARY OF THE INVENTION

The present invention relates to a method for the treatment of contaminated soil, sediment, clay, rock, and the like (hereinafter collectively referred to as "soil") containing volatile organic compounds, semi-volatile organic compounds,

pesticides and herbicides, as well as the treatment of contaminated groundwater (i.e., water found underground in cracks and spaces in soil, sand and rocks), process water (i.e., water resulting from various industrial processes) or wastewater (i.e., water containing domestic or industrial waste, often referred to as sewage) containing these compounds.

The method of the present invention uses one or more water soluble oxidants in combination with a pH modifier, where the pH modifier maintains a pH in the range of 6 – 10, under conditions which enable oxidation of most, and preferably substantially all, the organic compounds in the soil, groundwater, process water and/or wastewater, without the deleterious effects of metal mobilization or oxidant decomposition.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig 1is a diagram showing the relationship between the mole ratio of carbonate to persulfate ions; catalyst level and pH

Fig 2 is a graph showing pH as a function of the mole ratio of carbonate to persulfate ions.

Fig 3 is a diagram showing the loss of persulfate as a function of catalyst and carbonate levels

Fig 4 is a graph showing persulfate stability as a function of pH

Fig 5 is a diagram showing residual VOC's as a function of carbonate and catalyst levels.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the process of the present invention, organic compounds are oxidized by contacting the organic compound with a composition comprising (a) a water soluble peroxygen compound and (b) a pH modifier – i.e., any compound which is capable of stabilizing the pH, or buffering, the composition in its intended environment.

The oxidant may be any solid phase water soluble peroxygen compound, introduced into the soil or water in amounts, under conditions and in a manner which assures that the oxidizing compound is able to contact and oxidize most, and preferably substantially all, the target compounds.

In a preferred embodiment of the invention a composition comprising sodium carbonate and a peroxygen compound is introduced into the soil in sufficient quantities to satisfy the soil oxidant demand, compensate for decomposition, and to oxidize the target compounds. The quantity that needs to be added to control the pH in thae range of 6 to 10 is less than the stoichiometric requirement. On a stoichiometric basis each part of persulfate used requires one part of sodium carbonate to neutralize the acid produced. This equates to a mole ration of 1:1.

The use of carbonate to modify the pH of a peroxygen oxidant such as persulfate is an unanticipated result. Carbonate is a known radical scavenger and interferes with the ability of hydroxyl radicals to oxidize organics. ("Photocatalytic degradation of aqueous organic solvents, in the presence of hydroxyl radical scavengers, "Mehrab Mehrvar,William A. Anderson, and Murray Mòo-Young, International Journal Of Photoenergy 2001; Chemical Models of Advanced Oxidation Processes, William H. Glaze, Fernando Beltran, Tuula Tuhkanen and Joon-Wun Kang, Water Pollution Research Journal of Canada, 27(1): 23-42 (1992)).It would be expected that carbonate would also inhibit the reactivity of sulfate radicals.

This pH modification methodology may also be used ex situ to treat quantities of contaminated soil which have been removed from the ground.

According to another aspect of the present invention, under conditions where metal cations are present in the contaminated soil or water, the persulfate and carbonate composition may be introduced into the contaminated soil to remove the target compounds. The metal cations catalytically decompose the persulfate to form

sulfate free radicals, which oxidize the target VOCs. If the metal cations are not naturally present in sufficient quantities, they may be added from an external source. Such metal cations include divalent transition metals such as Fe^{+2}. Also, chelated metal ions, such as Fe^{+3} chelated with EDTA, where the chelant provides enhanced stability and solubility of the metal ion, may be added.

As per another aspect of the present invention, the persulfate and carbonate composition may be introduced into the soil, followed by heating of the soil to active the persulfate free radicals. Likewise, the persulfate and carbonate composition may be introduced into soil that has already been pre-heated for activation of persulfate free radicals.

In one embodiment of the present invention, the oxidation of organic compounds at a contaminated site is accomplished by the injection of a combination of persulfate and a carbonate into the soil.

In a preferred form of the invention, sodium persulfate (Na.sub.2 S.sub.2 O.sub.8) is introduced into the soil.

For in situ soil treatment, injection rates must be chosen based upon the hydrogeologic conditions, that is, the ability of the oxidizing solution to displace, mix and disperse with existing groundwater and move through the soil. Additionally, injection rates must be sufficient to satisfy the soil oxidant demand and chemical oxidant demand in a realistic time frame and to compensate for any decomposition of the oxidant. It is advantageous to clear up sites in both a cost effective and timely manner. Careful evaluation of site parameters is crucial. It is well known that soil permeability may change rapidly both as a function of depth and lateral dimension. Therefore, injection well locations are also site specific. Proper application of any remediation technology depends upon knowledge of the

subsurface conditions, both chemical and physical, and the present process is not different in that respect.

While sodium persulfate is the preferred peroxygen compound for oxidizing soil constituents, other solid phase water soluble peroxygen compounds can be used. By "solid phase water soluble peroxygen compound" it is meant a compound that is solid and water soluble at room temperature and contains a bi-atomic oxygen group, O--O. Such compounds include all the dipersulfates, monopersulfates, peroxides, and the like, with the dipersulfates being preferred because they are inexpensive and survive for long periods in groundwater saturated soil under typical site conditions.

The most preferred dipersulfate is sodium persulfate as it has the greatest solubility in water and is least expensive. Moreover, it generates sodium and sulfate upon reduction, both of which are relatively benign from environmental and health perspectives. Potassium persulfate and ammonium persulfate are examples of other persulfates which might be used. Potassium persulfate, however, is an order of magnitude less soluble in water than sodium persulfate; and ammonium persulfate is even less desirable as it may decompose into constituents which are potential health concerns.

In addition to sodium carbonate, examples of other pH modifiers that may be used include calcium carbonate, sodium bicarbonate, sodium and potassium phosphate, potassium carbonate, potassium bicarbonate, sodium sesquicarbonate, potassium sesquicarbonate, sodium borate, and TRIS buffer (Tris Hydroxymethylaminoethane). The weight ratio of persulfate to carbonate may be varied over a wide range depending upon the soil conditions and final target pH. A preferred ratio is 90 parts of persulfate and 10 parts of sodium carbonate which is less than the stoichiometric requirement for acid neutralization. It is also preferred to combine the persulfate and carbonate as a dry blend prior to shipment to the site where the composition is to be used. Thus it is desirable that the solid pH modifier be stable and non-hydroscopic. The carbonate/bicarbonate modifiers have such

properties. However, it is also possible to combine the two ingredients to prepare the composition at the site. Alternatively, the persulfate and the pH modifier may be injected sequentially at the site and the composition formed in situ.

The persulfate and pH modifier, being compatible with each other, may be mixed together and shipped or stored prior to being combined with water in the same vessel prior to injection. It is preferred that enough persulfate is present to satisfy substantially all the soil oxidant demand and to destroy the target compounds to acceptable levels, or as close thereto as possible, and enough pH modifier is present to maintain a pH between 6 and 8.

Depending upon the type of soil, target compounds, and other oxidant demand by the site, the concentrations of persulfate used in the present invention may vary from 0.5 g/L to greater than 250,000 mg/L. The preferred concentrations are a function of the soil characteristics, including the site-specific oxidant demands. Hydrogeologic conditions govern the rate of movement of the chemicals through the soil, and those conditions must be considered together with the soil chemistry to understand how best to perform the injection. The techniques for making these determinations and performing the injections are well known in the art. For example, wells or borings can be drilled at various locations in and around the suspected contaminated site to determine, as closely as possible, where the contamination is located. Core samples can be withdrawn, being careful to protect the samples from atmospheric oxidation. The samples can then be used to determine soil oxidant demand and chemical (e.g. VOC) oxidant demand and the oxidant stability existing in the subsurface. The precise chemical compounds in the soil and their concentration can be determined. Contaminated groundwater can be collected. Oxidants can be added to the collected groundwater during laboratory treatability experiments to determine which compounds are destroyed, in what order and to what degree, in the groundwater. It can then be determined whether the same oxidants are able to destroy those chemicals in the soil environment.

One method for calculating the preferred amount of peroxygen compound to be

used per unit soil mass (for an identified volume of soil at the site) is to first determine the minimum amount of persulfate needed to fully satisfy soil oxidant demand per unit mass of uncontaminated soil. A contaminated soil sample from the identified volume of soil is then treated with that predetermined (per unit mass) amount of persulfate; and the minimum amount of peroxygen compound required to eliminate the organic compounds in that treated sample is then determined. Chemical reaction stoichiometry governs the mass/mass ratios and thus the total amount required to achieve the desired result. In actuality the amount of peroxygen compound injected into various locations at a single contaminated site will vary depending upon what is learned from the core samples and other techniques for mapping what is believed to be the subsurface conditions.

The goal is for the concentration of peroxygen compound in the injected solution to be just enough to result in the peroxygen compound reaction front traveling throughout the area of contamination requiring treatment in sufficient quantity to oxidize the contaminants present. (The saturated soil zone is the zone of soil which lies below the water table and is fully saturated. This is the region in which groundwater exists and flows.) In certain saturated soil zones where the natural velocity of the groundwater is too slow for the purposes of treatment within a certain timeframe, the velocity of groundwater can be increased by increasing the flow rate of the injected solution or installation of groundwater extraction wells to direct the flow of the injected peroxygen compound solution. Certain soils to be treated may be in unsaturated zones and the method of peroxygen compound injection may be based on infiltration or trickling of the peroxygen compound solution into the subsurface to provide sufficient contact of the soils with the injected chemicals. Certain soils and conditions will require large amounts of peroxygen compound to destroy soil oxidant demand, while other soils and conditions might not. For example, sandy soils having large grain size might have very little surface area, very little oxidizable compounds and therefore very little soil oxidant demand. On the other hand, silty or clayey soils, which are very fine grained, would have large surface area per unit volume. They are likely to also

contain larger amounts of oxidizable compounds and thus have a higher overall soil oxidant demand.

The amount of pH modifier used in the present invention may vary from those having a mole ratio of carbonate ion to persulfate ion of from greater than 0.01 to less than 1.0 (the theoretical stoichiometric requirement). Preferred results are achieved with a carbonate ion to persulfate ion mole ratio of from 0.10 to 0.30.

In addition to in situ applications the process may also be employed ex situ. In addition to soil it may be used to treat sludges, sands, tars, groundwater, wastewater, process water or industrial water.

Another exemplary form of the invention is useful for destroying relatively low level, but unacceptable, concentrations of organic compounds in groundwater.

In order to describe the invention in more detail, the following examples are set forth:

EXAMPLE 1

Solid sodium persulfate, sodium carbonate and activator (Fe(II) or Fe-EDTA) were added to 40 mL brown glass vials at the appropriate masses to obtain targeted concentrations

Distilled water was added to the vial to contain zero headspace and the vial was capped with a teflon lined silicon rubber screw top to prevent volatile loss

A mixture of the volatile organic compounds (in methanol) was injected through the septum of the sealed vials into the water/oxidant/activator mixture.

Controls were constructed, without the addition of sodium persulfate, identical to the reaction vials

All vials were reacted at room temperature for 7 days.

Following 7 day reaction period, vials were stored at 4 deg C for analysis.

Analyses were performed on a gas chromatograph/mass spectrometer utilizing USEPA SW-846, Method 8260B

Reaction data were compared to control data in order to factor out any non-oxidative (i.e., volatile) losses that may have occurred

The % reduction of organics results are shown in the following table

	Percent Reduction Relative to Control				
% reduction	Fe II, CO3	Fe II	Fe-EDTA, CO3	Fe-EDTA	Carbonate Only
VC	100		100		0
1,1-DCE	100	100	100	100	2.83
MTBE	93.9	85.4	45.9	50.7	0
n-Hexane	98.9		94.5		0
cis-DCE	99.5	100	100	100	0
Chloroform	73.8	0	24.3	0	0
TCA	23.1	0	38.2	0	0
Benzene	100	100	100	98.8	0
TCE	98.8	100	100	100	1.9
Toluene	100	100	100	100	0
PCE	100	100	100	73.6	9.9
chlorobenzene	100	100	100	100	1.9
Methylene Cl	94.8	8.3	90.2	0	6.6
pH (Control 6.4)	9.9	2.2	8.5	2.3	11.2

It can be seen in this example that addition of carbonate to the sample maintains a higher pH than those samples without the buffer, without reducing the overall efficacy of the persulfate. In a couple of cases, addition of carbonate actually enhance the decomposition of the target organic compound. This is unexpected as carbonate is known to be a radical scavenger and decreases the reactivity of hydroxyl radicals.

EXAMPLE 2

An experiment was conducted to determine the levels of buffer to add to a VOC containing solution being dosed with sodium persulfate. 40 mL brown glass vials were dosed with a stock contaminate solution containing the following compounds in methanol: chlorinated ethenes (tectrachloroehane, trichloroethene, cis-1,2-dichloroethene, 1-1-dichloroethene, vinyl chloride), aromatics (benzene, toluene, chlorobeneze), chloroform, 1,1,1-trichloroethane, n-hexane, and methyl-tert-butyl ether. To this solution was added 3.95 g of sodium persulfate, representing a two-fold stoichiometric dose for all of the organics. Catalyst (Fe-EDTA) and sodium carbonate were added in varying amounts. Analyses were performed on a gas chromatograph/mass spectrometer utilizing USEPA SW-846, Method 8260B. Comparisons were made between untreated (no persulfate) levels of contaminant and treated levels.

In the trials where no buffer was added, the pH of the sample vials were all below 2. Figure 1 shows the relationship between measured pH after seven days of reaction and the mole ratio between carbonate and persulfate as well as catalyst (Fe-EDTA) level. From the figure, the 7th day pH is most strongly dependent upon the carbonate to persulfate ratio. A carbonate to persulfate ratio of 0.1 to 0.5 results in a pH range of 4.5 to 9.0. Figure 2 displays the relationship of pH to mole ratio of carbonate to persulfate, removing the effects of the catalyst level. As can be seen, there is a “breakpoint” in the pH response at a carbonate to persulfate mole ration of about 0.2. The pH modification response holds true for catalyzed (Fe-EDTA) and uncatalyzed persulfate.

The amount of persulfate remaining was determined after 3 and 7 days. Although the loss of persulfate due to either reaction with the VOC's or through non-productive decomposition was not distinguishable, a correlation was determined between the average percent of VOC's removed and the amount of persulfate remaining. The correlation was 79% for the three-day results and 74% for the seven-day results. This suggests that the greater the loss of persulfate the poorer the oxidation of the VOC's, indicating that minimizing the loss of persulfate through decomposition will improve the oxidative performance.

Figure 3 shows the loss of persulfate after seven days as a function of catalyst (Fe-EDTA) loading and carbonate loading. From this figure it can be seen that there is a strong correlation between catalyst loading and persulfate loss (98% correlation).. The effect of carbonate loading was dependent upon catalyst level. At catalyst levels below 150 mg / L Fe, the addition of carbonate had a general positive effect on persulfate loss. At high levels of catalyst loading (> 300 mg/L Fe), reducing the level of carbonate, or going to high levels of carbonate were beneficial, while intermediate amounts were generally worse. Figure 4 shows the effect of carbonate loading averaged over all trials where the catalyst loading was 100 mg / L Fe or less. From the figure, it can be seen that below a carbonate to persulfate ratio of 0.2, the persulfate stability is degraded, and at ratios greater than 1.0, the stability also begins to decrease. Thus the addition of carbonate at the proper levels will improve the persulfate stability.

EXAMPLE 3

This study was run essentially the same as Example 2. However the contaminants were dispersed in water as compared to methanol, and the number of contaminants were increased. The contaminants included: tetrachloroethane, trichloroethene, cis-1,2-dichlorethene, trans-1,2-dichloroethene, 1,1-dichloroethene, 1-1-dichloroethane, 1,2-dichlorethane, 1,1,1-trichloroethane, carbon tetrachloride, methylene chloride, chloroform, benzene, toluene, m,p,o-xylene, chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,2,4-trichlorobenzene, 1,4-dioxane,

tertbutyl alcohohol, MTBE and 4-methyl-2-pentanone. Sodium persulfate was added to meet twice the stoichiometric demand of oxidizing all of the VOC's, and catalyst (Fe-EDTA) and sodium carbonate were added in varying amounts.

There was a 98% correlation between pH and carbonate to persulfate ratio after seven days. The following table displays the resultant pH.

Carbonate to Persulfate ratio	0	0.1	0.2	0.3
pH after 7 days	2.0	7.6	8.5	9.3

Figure 5 shows the total residual VOC's after seven days of reaction time. The total initial VOC concentration was 329 mg / L. Optimal conditions for 100 mg / L Fe catalyst result in a carbonate to persulfate ratio of 0.15 – 0.20. For 300 mg / L Fe, the optimal carbonate to persulfate ratio is 0.25 – 0.30. This demonstrates that the addition of carbonate to a persulfate solution allows less catalyst to be used. Reducing the amount of catalyst has several beefits. First it improves the stability of the persulfate. Second it lowers the cost of the application.